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Sodium diphenylacetate, an infinite columnar structure

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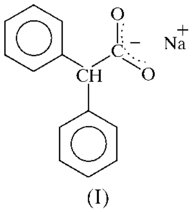
In the title compound, $Na^+\cdot C_{14}H_{11}O_2^-$, the diphenylacetate ions have a conformation where the two phenyl rings and the carboxylate group are oriented like the blades of a propeller, each ion having a well defined helicity. The crystal structure of the title compound is achiral, although non-centrosymmetric (space group $P\bar{4}2_1c$); thus, ions with both (+) and (−) helicities are present in the crystal. Each Na^+ ion is coordinated by four carboxylate O atoms at distances in the range 2.207 (2)–2.467 (3) Å to form cubes of Na and O atoms which are linked *via* the carboxylate C atoms into a columnar structure along the rotoinversion axis.

Comment

The molecule of diphenylacetic acid is achiral, but due to the rotational mobility of the phenyl rings the molecule may assume a helical chiral conformation where the two phenyl rings and the carboxylate group are oriented like the blades of a propeller. When forming molecular compounds with other achiral molecules, such a conformation can induce a chiral crystal structure. An interesting example of this situation occurs in the 1:1 adduct of diphenylacetic acid and acridine, which crystallizes from acetonitrile in a chiral crystal structure (space group $P2_12_12_1$) and spontaneously resolves the (+) and (−) enantiomers (Koshima *et al.*, 1996). This compound is photoreactive and has been used in absolute asymmetric synthesis by photodecarboxylating condensation performed in the solid state. Our interest in this type of absolute asymmetric synthesis led us to a systematic study of other compounds of diphenylacetic acid, including the title compound, sodium diphenylacetate, (I), whose structure is reported here. According to a search of the Cambridge Structural Database (CSD release April 1999; Allen & Kennard, 1993), this is the first reported crystal structure of a salt of diphenylacetic acid with an alkali metal.



(I)

Compound (I) crystallizes in the achiral, although non-centrosymmetric, space group $P\bar{4}2_1c$ (Jones, 1986) and both enantiomers of the helical conformation of the diphenyl-

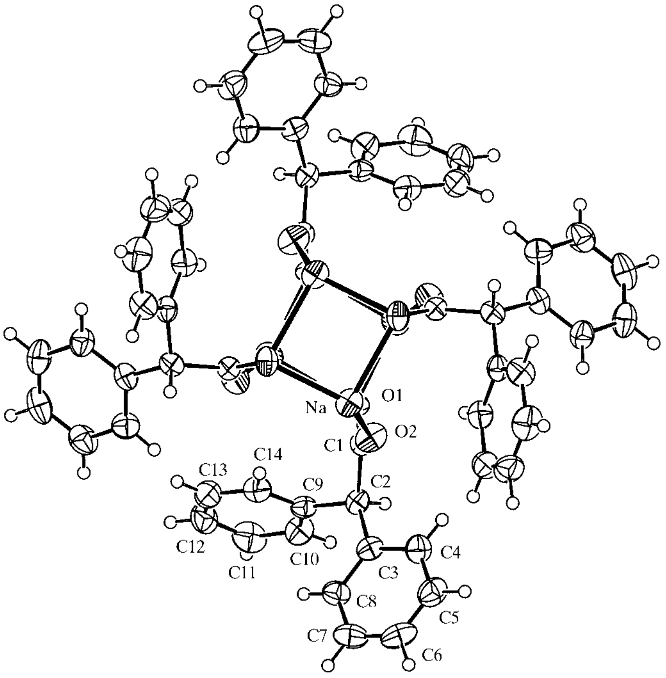


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I) viewed along the $\bar{4}$ axis (*c* axis). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

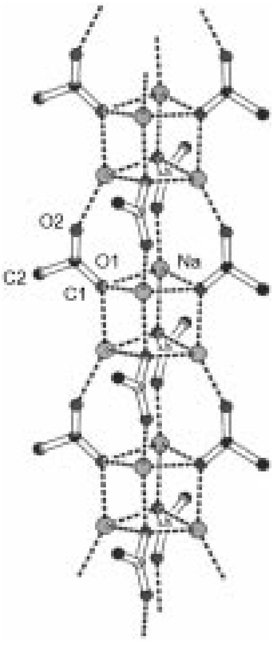


Figure 2
Stacking of the Na/O core along the *c* axis showing the columnar structure. The phenyl groups have been omitted for clarity.

acetate ion are present in the unit cell. There is an ambiguity in the absolute assignment of the x and y axes in such a high symmetry non-centrosymmetric space group which can only be resolved if a sufficiently strong anomalous scatterer is present. In fact, inverting the structure in $P\bar{4}2_1c$ is equivalent to the interchange of axes $x \rightarrow y$ and $y \rightarrow x$. However, due to the low value of the anomalous dispersion of all atoms, including Na, at the Mo $K\alpha$ wavelength, it was not possible to resolve in the present case the ambiguity in the absolute assignment of the x and y axes.

The coordination of the diphenylacetate ions around the metal ions is shown in Fig. 1 and Fig. 2. The carboxylate O1 atom and the Na^+ ions alternate at the vertices of a distorted cube centered at the origin of the $\bar{4}$ axis. Each Na^+ ion is coordinated by four O atoms (one O2 atom outside the cube and three O1 atoms at adjacent vertices of the 'cube') at distances in the range 2.207 (2)–2.467 (3) Å. These distances are close to the average Na^+O^{2-} distance [2.44 (16) Å; Bergerhoff & Brandenburg, 1995], except for the $Na—O2^i$ [symmetry code: (i) $y, x, -z$] distance [2.207 (2) Å], which is somewhat shorter. The Na/O core forms a columnar structure along the $\bar{4}$ axis, as seen in Fig. 2. The distorted cubes of Na and O1 atoms alternate along the columns, with the carboxylate groups, which act as bridges, joining adjacent cubes. Interestingly, the carboxylate O2 atom is involved solely in the bridging, while the O1 atom and its symmetry-related counterparts make up the oxygen content of the cube construction.

The carboxylate skeleton defined by atoms C1, C2, O1 and O2 is planar to within 0.003 Å. There is significant asymmetry between the bond distances C1—O1 [1.271 (3) Å] and C1—O2 [1.226 (3) Å], which deviate significantly from the average value of a typical delocalized double bond in carboxylate anions [1.254 (10) Å; Allen *et al.*, 1987]. The asymmetry between these two bonds is probably explained by the different environments of the O1 and O2 atoms, O1 having three Na^+ ions as near neighbours, while O2 has just a single alkaline ion in the first coordination shell. This may also induce the large asymmetry between the angles C2—C1—O1 [113.6 (2)°] and C2—C1—O2 [121.4 (3)°]. However, the angle O1—C1—O2 [125.0 (3)°] is typical for a carboxylate group. The shortest distance between two metal ions is 3.265 (2) Å, which greatly exceeds the sum of two ionic radii of Na^+.

The dihedral angle between the least-squares planes of the two phenyl rings is 89.35 (16)°. The dihedral angles between each of the rings and the bridging plane defined by atoms C2, C3 and C9 are 5.0 (3) (C3–C8) and 84.4 (3)° (C9–C14). The carboxylate group makes an angle of 56.7 (3)° with the bridging plane and angles of 54.61 (16) and 78.40 (17)° with rings C3–C8 and C9–C14, respectively. The two phenyl rings and the carboxylate plane have torsions around the single bonds to C2 in the same direction, like the blades of a propeller. This is confirmed by examining the torsion angles around C2 [H2—C2—C1—O1 58.0, H2—C2—C3—C4 62.5 and H2—C2—C9—C10 21.8°], which all have the same sign. These torsion angles should be compared with the corresponding values in the molecular crystal of diphenylacetic acid (48.2, 27.3 and 52.8°, respectively; Koshima *et al.*, 1996) and in the 1:1 adduct of diphenylacetic acid and acridine (33.9, 50.3 and 13.0°, respectively; Koshima *et al.*, 1996). This shows that the phenyl and carboxylate groups may rotate rather freely around the single bonds joining them to the central C atom. Indeed, there is evidence that these groups are sufficiently mobile in solution to allow inversion of helicity (Koshima *et al.*, 1996).

There are no classical hydrogen bonds in this structure. Cohesion is maintained mainly by electrostatic forces and weaker van der Waals interactions. Interaction between π-clouds and metal atoms does not appear to play a major role, the shortest ring–metal distance being 3.812 (5) Å. There is, however, a relatively short distance between the H atom attached to C10 and the C3–C8 phenyl ring [2.847 (5) Å].

Experimental

Compound (I) was prepared by neutralizing an ethanolic solution of diphenylacetic acid (98%, Aldrich) with sodium hydroxide. Clear transparent single crystals of prismatic form grew from the solution by slow evaporation over a period of a few weeks, from which one small crystal was selected and used for the X-ray analysis. Before data collection, the quality of the crystal was checked by photographic methods.

Crystal data

$Na^+\cdot C_{14}H_{11}O_2^-$
$M_r = 234.22$
Tetragonal, $P\bar{4}2_1c$
$a = 18.944$ (3) Å
$c = 6.3326$ (11) Å
$V = 2272.6$ (6) Å^3
$Z = 8$
$D_x = 1.369$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.99$–$13.94°$
$\mu = 0.123$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.24 × 0.24 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.923$, $T_{max} = 0.982$
2596 measured reflections
1598 independent reflections
1135 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 27.43°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 24$
$l = -6 \rightarrow 8$
3 standard reflections
frequency: 180 min
intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.106$
$S = 1.076$
1598 reflections
154 parameters
H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.4591P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.204$ e Å^{-3}
$\Delta\rho_{min} = -0.169$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

$Na—O2^i$	2.207 (2)	$Na—O1^{iii}$	2.467 (3)
$Na—O1$	2.316 (2)	$Na—Na^{iii}$	3.265 (3)
$Na—O1^{ii}$	2.344 (2)	$Na—Na^{iv}$	3.476 (2)
$O2^i—Na—O1$	119.12 (9)	$O2^i—Na—O1^{iii}$	107.87 (9)
$O2^i—Na—O1^{ii}$	149.79 (10)	$O1—Na—O1^{iii}$	92.63 (9)
$O1—Na—O1^{ii}$	87.14 (8)	$O1^{ii}—Na—O1^{iii}$	83.72 (8)

Symmetry codes: (i) $-y, x, 1 - z$; (ii) $-y, x, -z$; (iii) $-x, -y, z$; (iv) $y, -x, -z$.

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Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1088). Services for accessing these data are described at the back of the journal.

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